A Theoretical Thermodynamic Study of Heat Transmission in Interstitial Solid Solutions and in Solid-State Semiconductors.

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(I) Introduction

Creation of a concentration gradient in a solution by imposing a temperature gradient has long known as thermal diffusion. Recently, some measurements of the magnitude of this effect in solid solution alloys have been made. Shewmon has shown that an appreciable effect occurs only in systems where the migrating species has a diffusivity of greater than 10^{-9} cm^2/sec. In the case of substitutional solid solutionds, a diffusivity of this magnitude is only attained at temperatures very near the melting point of the material. Interstitial solute diffusivities, on the other hand, are often much larger than this value at temperatures where the matrix material is commonly used. Since examples of such alloy systems include Fe–C, Zr–H, and Fe–N, the effect of thermal diffusion in interstitial solid solutions may be of great interest.

In most thermal diffusion experiments where a solution is under a temperature gradient, the solute solubility varies significantly over the temperature range in which the system is held, It might be expected, then that the observed diffusion is at least partially influenced by solubility differences. This might be true even if the steady-state solute distribution did not remotely resemble the temprature-solubility curve. Accordingly, it is of interest to see whether an explicit relation incorporating the solubility effect can be derived. We have found it possible to do this in the case of interstitial solid solutions.

The redistribution of an interstitial solute under a temperature gradient can be described with the aid of the discipline of irreversible thermobynamics. Denbigb's treatment, based on the works of Onsager and de Groot, has shown that diffusion is a two-component system under a temperature gradient may be described in terms of the following Set of phenomenological equations.

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{1H}X_H \quad \cdots\cdots(1)$$
$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{2H}X_H \quad \cdots\cdots(2)$$
$$J_H = L_{H1}X_1 + L_{H2}X_2 + L_{HH}X_H \quad \cdots\cdots(3)$$

Where J_j = flux of component "i",
J_H = thermal energy flux,
X_i = material driving force due to component "i",
X_H = thermal driving force,
L_{11}. L_{22} = component diffusivities,
L_{HH} = thermal conductivity,

The other L coefficients are cross coefficients, representing couplings among the heat and material flows.

(Ⅱ) Treatment for Interstitial Solid Solution Systems

In the case of thermal diffusion of a solute through a stationary solvent lattice, where J_2 is equal to zero, from this, equation (2) reduces to

$$-L_{22}X_2 = L_{21}X_1 + L_{2H}X_H \quad \cdots\cdots(4)$$

Multiplying equation (4) by $-\frac{L_{12}}{L_{22}}$ and substituting into equation (1), we have

$$J_1 = \left(L_{11} - \frac{L_{12}L_{21}}{L_{22}}\right)X_1 + \left(L_{1H} - \frac{L_{12}L_{2H}}{L_{22}}\right)X_H \quad \cdots\cdots(5)$$

again multiplying equation (4) by $-\frac{L_{H2}}{L_{22}}$ and substituting into equation (3), we get

$$J_H = \left(L_{H1} - \frac{L_{H2}L_{21}}{L_{22}}\right)X_1 + \left(L_{HH} - \frac{L_{H2}L_{2H}}{L_{22}}\right)X_H \quad \cdots\cdots(6)$$

Hence, we may write a set of phenomenological relations for J_1 and L_H in terms of X_1 and X_H :